Molecular Size Distribution in Linear Condensation Polymers[1]
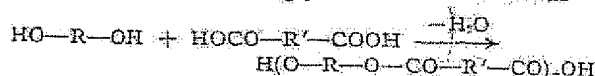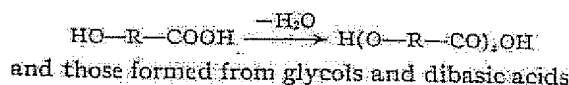
BY PAUL J. FLORY

Introduction

All synthetic polymers and most natural ones are recognized to be non-homogeneous substances consisting of mixtures of chemically similar molecules which are distributed in size about an average, some of them being much smaller and some much larger than this average. By various methods, more or less approximate estimates of the average molecular weights of such materials can be made, but as yet information concerning the distribution of molecules amongst the various sizes is exceedingly meager. An adequate understanding of the fundamental nature of polymeric substances requires comprehension of the molecular size distributions as well as the empirical compositions and average molecular weights.

Methods have been developed for the experimental determination of molecular size distributions in polymers by using the Svedberg ultracentrifuge,[2] but they have so far been applied only to a limited extent. Theoretical calculation of the molecular size distribution is possible if the kinetic mechanism of the polymerization process is sufficiently well understood. Such calculations have been attempted for vinyl polymerizations by Chalmers,[3] by Dostal and Mark,[4] and more recently by Schulz.[5]

The present paper offers a theoretical analysis of the molecular size distribution in linear condensation polymers formed by the inter-molecular reaction of bifunctional compounds. The polyesters prepared by Carothers and co-workers[6] provide excellent examples of this type of polymer. They are of two kinds, those formed from hydroxy acids
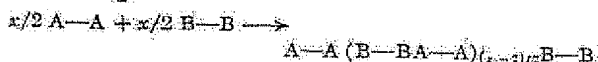
$$HO-R-COOH \xrightarrow{-H_2O} H(O-R-CO)_xOH$$

and those formed from glycols and dibasic acids

$$HO-R-OH + HOCO-R'-COOH \xrightarrow{-H_2O}$$
$$H(O-R-O-CO-R'-CO)_xOH$$

In general, polymerizations[7] of the first type above may be formulated as

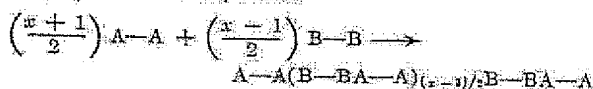(i) $x A-B \longrightarrow A-B (A-B)_{x-2} A-B$

where A and B represent functional groups and AB, or BA, the product of their reaction with one another. A simple molecule such as water may or may not be released in this process. If, as in the second example above, there are two kinds of reactants, A—A and B—B, three varieties of molecules may be formed in the polymeric mixture, viz.,
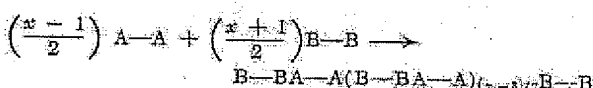
(iia) If x, the total number of reactant molecules combined in the polymer molecule, is an even integer

$x/2$ A—A $+ x/2$ B—B $\longrightarrow$
$$A-A (B-BA-A)_{(x-2)/2} B-B$$

(iib) If x is odd, either

$\left(\dfrac{x+1}{2}\right) A-A + \left(\dfrac{x-1}{2}\right) B-B \longrightarrow$
$$A-A(B-BA-A)_{(x-1)/2} B-BA-A$$

or

$\left(\dfrac{x-1}{2}\right) A-A + \left(\dfrac{x+1}{2}\right) B-B \longrightarrow$
$$B-BA-A(B-BA-A)_{(x-3)/2} B-B$$

Another case which might be considered is that in which the functional groups are all alike, but this may be taken as a special case of (i) in which A = B.

It is characteristic of all of these polymerizations that they involve the coupling of two bifunctional compounds to form a bifunctional compound of higher molecular weight, which in turn is capable of polymerizing with other molecules. Here the reactions: monomer with monomer, monomer with polymer, and polymer with polymer all involve the same chemical process. These condensation polymerizations are not to be confused with polymerizations proceeding by a chain mechanism, for example, vinyl polymerizations,[8] or

(1) A preliminary account of part of this work was included in a paper presented by Dr. Wallace H. Carothers before the Faraday Society Symposium, September, 1935 [Trans. Faraday Soc., 32, 39 (1936)].

(2) (a) Svedberg, Chem. Rev., 14, 1 (1934). (b) Signer and Gross, Helv. Chim. Acta, 17, 726 (1934), and Signer, Kolloid Z., 70, 24 (1935), have calculated size distributions for polystyrenes from sedimentation velocities in the ultracentrifuge. (c) Lansing and Kraemer [THIS JOURNAL, 57, 1369 (1935)] have derived methods for calculating a "non-uniformity coefficient" from determination of the sedimentation equilibrium distribution of a polymeric material in the ultracentrifuge.

(3) Chalmers, ibid., 56, 912 (1934).

(4) Dostal and Mark, Z. physik. Chem., B29, 299 (1935).

(5) Schulz, ibid., B30, 379 (1935).

(6) Carothers, Chem. Rev., 8, 359-98 (1931).

(7) The reasons for classing bifunctional condensations such as these as true polymerizations have been set forth by Carothers.[6]

(8) Semenoff, "Chemical Kinetics and Chain Reactions," Oxford Univ. Press, Oxford, England, 1935, p. 444.

the polymerization of formaldehyde catalyzed by formic acid.[8]

The treatment which follows rests upon the fundamental assumption that the reactivity of a functional group, A or B, is independent of the size of the molecule to which it is attached. If the functional groups are separated by more than three atoms in the chain, this assumption is probably not seriously in error; if only one or two atoms separate the functional groups in the monomer, then the reactivities of monomer and dimer may differ greatly although the difference between dimer and trimer will be much less, between trimer and tetramer still less, etc.[10] If the reverse reaction, polymer degradation, occurs appreciably, it is necessary to append the assumption of equal reactivity of all links, AB, with respect to the reverse reaction, e. g., hydrolysis in the case of polyesters. It is also assumed that the formation of cyclic compounds (as well as other side reactions) does not occur to an appreciable extent.[11] The errors arising from the assumptions will in general be most significant in the range of low molecular weights; for polymers of high average molecular weight, where the distribution is broad and the low molecular weight portion is small, deviation from the calculated results should not be large.

Theoretical Treatment and Discussion

Type (i) polymers and type (ii) polymers formed from equivalents of A—A and B—B molecules can be subjected to the same treatment and so will be considered simultaneously. The special and more complicated problem of the size distribution relations in type (ii) polymers formed from non-equivalents of A—A and B—B molecules will be relegated to a separate later section.

Definitions.—A reactant molecule or its radical will be defined as a "segment" and the term

"x-mer" will denote a polymer composed of x segments, e. g., a hexamer is a polymer composed of six segments.[12]

The following notation will be used:

n_0 = total number of segments = total number of A (or B) groups.

N = number of unreacted A (or B) groups which remain after the reaction has been in progress for a time, t.
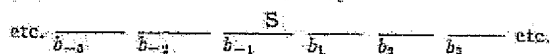
$N_0 - N$ = number of reacted A (or B) groups.

(If desired, the N's may be expressed in moles without altering any of the equations which follow.)

p, the extent of reaction, = fraction of the total number of A (or B) groups which have reacted at time t

$$p = (N_0 - N)/N_0 \qquad (1)$$

Fundamental Distribution Functions.—In order to derive the distribution functions, let us determine the probability, Π_x, that a particular segment selected at random is part of an x-mer. Picture a large group of partially polymerized segments laid end to end, thus

$$\text{etc.} \underset{b_{-3}}{\rule{1cm}{0.4pt}} \underset{b_{-2}}{\rule{1cm}{0.4pt}} \underset{b_{-1}}{\rule{1cm}{0.4pt}} \overset{S}{\underset{b_1}{\rule{1cm}{0.4pt}}} \underset{b_2}{\rule{1cm}{0.4pt}} \underset{b_3}{\rule{1cm}{0.4pt}} \text{etc.}$$

the b's designating the linkages, or potential linkages, between the segments. Since all unreacted functional groups are assumed to be equally reactive, the probability that reaction has occurred to link the segments at any particular b is p and the probability that no linkage exists is $1-p$. There are x possible configurations, such as for example that consisting of linkages at $b_1, b_2 \ldots b_{x-1}$ and unreacted functional groups at b_{-1} and b_x, which fulfill the condition that the segment S be part of an x-mer. Since each of these consists of $x-1$ linkages and two unreacted potential linkages, the probability of the existence of each particular configuration is $p^{x-1}(1-p)^2$. The probability that any of the x configurations exists is[13]

$$\Pi_x = x p^{x-1} (1 - p)^2 \qquad (2)$$

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(9) Carothers and Norrish, *Trans. Faraday Soc.*, **32**, 195 (1936).

(10) Factors which cause change in reaction rate during the course of the reaction do not invalidate this assumption if the rates of reaction of a monomer, a dimer, etc., are all affected equally. Thus, the increase in viscosity of the medium as the reaction progresses might slow down the reaction; but if the rate of reaction of each molecular species is slowed down proportionately the equality of the reactivities of all functional groups at any one time remains undisturbed.

(11) That the extent of ring formation in bifunctional esterifications involving unit lengths beyond 7 is exceedingly small has been shown experimentally in many papers published from this Laboratory—c. g., Carothers and Hill, THIS JOURNAL, **54**, 1561 (1932). More recently something in the nature of quantitative data on this point has become available in a paper by Stoll and Rouvé [*Helv. Chim. Acta*, **18**, 1087 (1935)]. By a long (and somewhat doubtful) extrapolation one can, for example, calculate that pure hydroxydecanoic acid would furnish only 0.0005% of monomeric lactone at complete esterification, while higher hydroxy acids might give us much as 0.2% of lactone.

(12) In condensations of type (i) a segment is identical with a "structural unit" as previously defined by Carothers [THIS JOURNAL, **51**, 2548 (1929); *ibid.*, **55**, 5023 (1933)], but in type (ii) condensations a segment is one A—A or one B—B group whereas the structural unit is A—AB—B. For type (ii) polymers the above definition of an x-mer does not agree with the previous definition according to which an x-mer contains x structural units. The above definitions have been adopted for the sake of simplifying the following analysis.

(13) Kuhn, *Ber.*, **63**, 1503 (1930), has derived the same equation for the molecular size distribution in a degraded cellulose formed by the hydrolysis of infinitely large cellulose molecules, assuming that all linkages are equally hydrolyzable. That the two distributions should be identical is obvious when one considers the equivalence of the formation of polymer molecules through random formation of linkages and through random breaking of linkages already formed. In a further study of the problem of cellulose degradation, Klages, *Z. physik. Chem.*, A159, 357 (1932), and Kuhn, *ibid.*, A159, 368 (1932), have taken into account the finite size of the cellulose molecule prior to its degradation, and they have deemed it necessary to consider different rates for mid-chain hydrolysis and for hydrolysis of the terminal unit. These added complications lead to results which differ from those for bifunctional condensations. Schulz's equation for the weight fraction distribution in vinyl

As a consequence of the definition of Π_x

$$\Pi_x = \frac{\text{Total number of segments which exist as components of } x\text{-mers}}{\text{Total number of segments } (= N_0)}$$

If in the condensation process no molecule such as water is eliminated, the molecular weight will be exactly proportional to the number of segments in the molecule, and Π_x will be exactly equal to the weight fraction of x-mers. If a molecule is eliminated in the condensation, the deviation from this proportionality (due to the excess weight of the unreacted terminal functional groups) will be negligible except for the very low molecular weight polymers. Hence, Π_x will be regarded hereinafter as the weight fraction.[14]

The number of x-mer molecules is given by

$$N_x = \frac{N_0 \Pi_x}{x} = N_0 p^{x-1}(1 - p)^2 \qquad (3)$$

Since there is an average of one A (or B) group per molecule, the total number of molecules $N = N_0(1 - p)$ (see (1)). Therefore, letting P_x be the mole fraction of x-mers

$$P_x = N_x/N = p^{x-1}(1 - p) \qquad (4)$$

In order to locate the x value which gives a maximum in Π_x, let

$$\partial \Pi_x/\partial x = (1 - p)^2 (p^{x-1} + x p^{x-1} \ln p) = 0$$

Solutions are, $x = \infty$ (minimum), and

$$x_{max.} = -1/\ln p \qquad (5)$$

which for values of p near unity becomes

$$x_{max.} \cong 1/(1 - p) = N_0/N = \text{average value of } x \qquad (5b)$$

At the maximum

$$\Pi_{max.} = -\frac{(1 - p)^2}{\ln p} e^{-(1 + \ln p)} \qquad (6)$$

which, on introducing approximations valid when p is near unity, becomes

$$\Pi_{max.} = (1 - p)/e \qquad (6b)$$

Differentiating P_x with respect to x and equating to zero

polymers is essentially the same as (2) also, although it is based on an entirely different set of conditions. His equation for the weight fraction of x-mer expressed in the symbols used in this paper is $xp^x (\ln p)^2$ where $1 - p$ ($1 - \alpha$ in Schulz's terminology) is the ratio of the velocity of chain termination to the velocity of chain propagation. Inasmuch as Schulz was interested only in large x values, he replaced $1 - x$ in the exponential. The constant term, $(\ln p)^2$, was evaluated by integration, a method which is approximate when applied to a mixture of molecules which vary in size in a stepwise manner. Had direct summation been used, this term would have been $(1 - p)^2$ as in (2). However, for values of p near unity $(1 - p)^2 = (\ln p)^2$.

(14) In type (ii) polymers it will be recalled that we have one type of x-mer when x is even and two when x is odd. When x is even the considerations of the preceding paragraph apply at once. When x is odd the numbers of the two types of x-mers are equal as a consequence of the assumption of equal reactivity of all A and of all B groups. It follows from this that if we take Π_x when x is odd to include both kinds of x-mers combined, then Π_x can be taken as the approximate weight fraction of x-mers in type (ii) as well as in (i) without further assumptions.

$$\frac{\partial P_x}{\partial x} = p^{x-1}(1 - p) \ln p = 0$$

Since $x = \infty$ is the only solution, P_x possesses no maximum with respect to x.

The values of p which will give respectively the maximum amount and the maximum number of a particular x-mer may be obtained as follows

$$\partial \Pi_x/\partial p = x p^{x-2}(1 - p)(x - 1 - px - p) = 0$$

for which solutions are $p = 0$, 1 or

$$p_{max.} = (x - 1)/(x + 1) \qquad (7)$$

Similarly

$$\frac{\partial P_x}{\partial p} = p^{x-2}(x - px - 1) = 0$$

$$p_{max.} = (x - 1)/x \qquad (8)$$

Discussion and Graphs.—The weight fraction distribution function (2) and the mole fraction distribution function (4) are represented graphically in Figs. 1 and 2 and in Figs. 3 and 4,
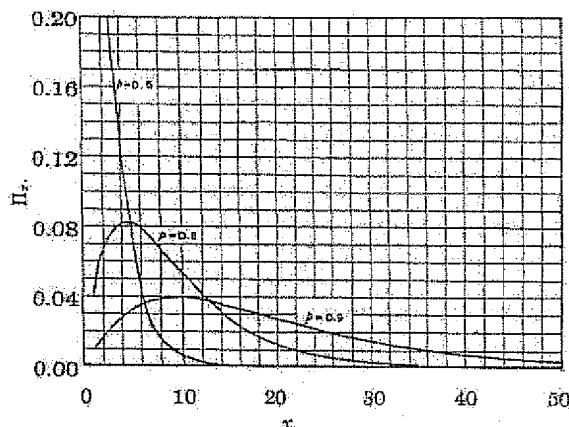

Fig. 1.—Weight fraction distributions for moderate extents of reaction (p). One square = 0.02 weight fraction.

respectively, for the several values of p indicated above each curve. From the curves in Figs. 1 and 2 one can determine the relative quantities (by weight) of each molecular species; the curves in Figs. 3 and 4 give the relative numbers of molecules of each species. For the smaller values of p the weight fraction curve possesses a sharp maximum, but as p approaches unity, this maximum becomes lower, shifted to larger values of x, and broader in the sense that there are more species present in approximately the maximum amount.[15]

(15) It can be shown that the curves in Figs. 2 and 4 may be used for larger values of p by altering the coördinate scale according to the following rule: if p be increased so that $1 - p$ is decreased n-fold, then the ordinate must be divided by n and the abscissa multiplied by n. Thus, the $p = 0.98$ curve may be used for $p = 0.998$ if the Π_x or P_x values be divided by ten and the x values multiplied by ten. This procedure is approximate, but the error is insignificant if p is ≥ 0.95 and $x \geq 20$.

The x-mer which is present in greater amount than any other, specified by the maximum in the Π_x curve, is given by (5) or (5b), and the quantity of this species is given by (6) or (6b). $x_{max.}$ coincides approximately with the average value of x (number-average, *cf. seq.*). It can be shown that for values of $p < 0.5$, monomer is in excess
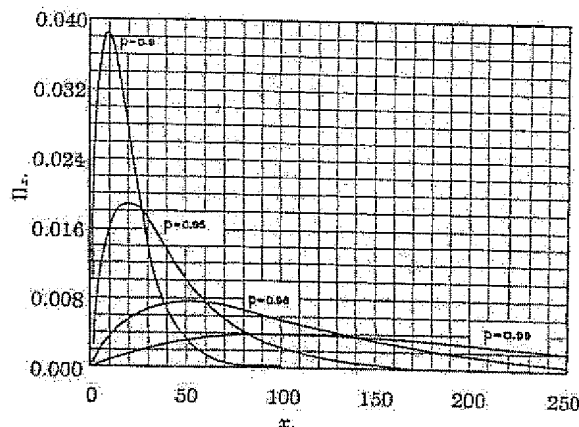

Fig. 2.—Weight fraction distributions for large extents of reaction. One square = 0.02 weight fraction.

(by weight) of any other species; for $p > 0.5$, $x_{max.} \geqq 2$. As is shown by the above analysis, there is no maximum in the P_x curve for any value of p (see Figs. 3 and 4), and so *there are always more molecules of monomer than of any other single species.*
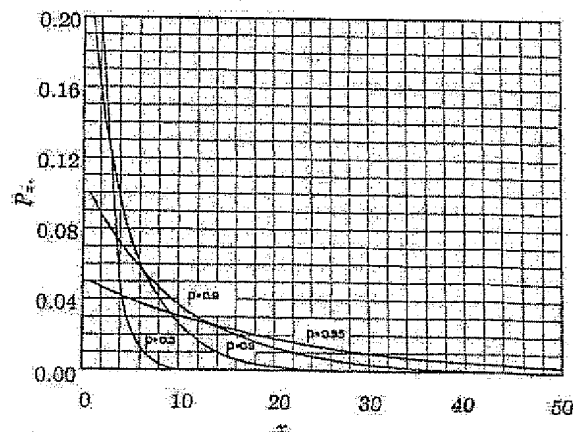

Fig. 3.—Mole fraction distributions for moderate extents of reaction (p). One square = 0.02 mole fraction.

In Fig. 5 the weight fraction is plotted against p for several values of x. As the reaction progresses, the amount of a particular x-mer builds up to a maximum located according to (7) at $p = (x - 1)/(x + 1)$ and then falls away to approach

zero as p approaches unity. As x is increased, the maximum is lowered and shifted to higher p values. The mole fraction of a particular x-mer increases in a similar (but not identical) way as the reaction progresses, reaches a maximum (equation (8)) and then decreases to zero as p approaches unity.
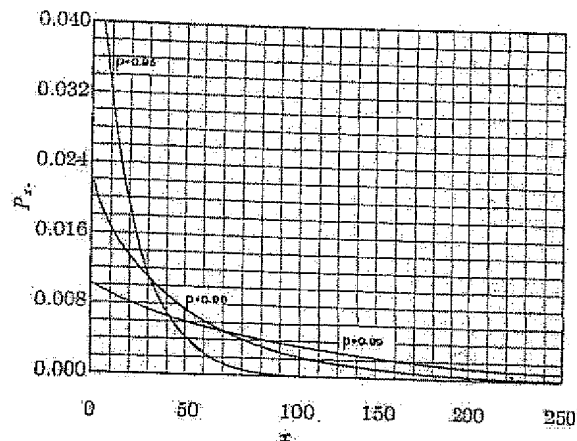

Fig. 4.—Mole fraction distributions for large extents of reaction. One square = 0.02 mole fraction.

The sum of the weight fractions of all constituents, of necessity always equal to unity, is approximately equal to the area under one of the curves in Figs. 1 and 2 from $x = 1$ to $x = \infty$, since[16]

$$\sum_{x=1}^{x=\infty} \Pi_x \cong \int \Pi_x \, dx$$

Similarly, the weight fraction of all constituents between $x = x_1$ and $x = x_2$ is approximately equal to the area under the curve from $x = x_1$ to
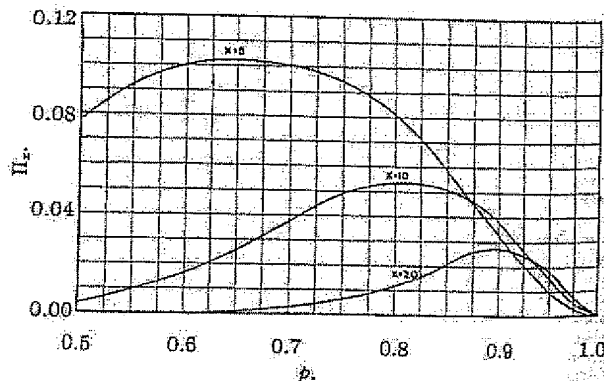

Fig. 5.—Weight fraction of x-mer vs. extent of reaction.

(16) The failure of this area to equal unity exactly arises because of the treatment of a discontinuous phenomenon as a continuous one; that is, only integral values of x have physical meaning, whereas the integration is carried out continuously over all values of x. When p is sufficiently large, however, the integral (or the area under the curve) differs inappreciably from unity.

$x = x_a$, and so the total weight fraction of these constituents can be evaluated graphically. This may be done in Figs. 1 and 2 by counting the squares under the curve between these limits and multiplying by 0.02. Similar considerations apply to the mole fraction graphs. This procedure is approximate, but for broad distributions ($p \geqq 0.90$) it may be used without significant error. For such distributions nearly three-fourths of the material (by weight) consists of molecules for which $x > x_{max} \cong$ average x.

Molecular Weight Averages.—Lansing and Kraemer[3c] have discussed three different kinds of average molecular weights which are amenable to physical measurement. These are defined by the equations

$$M_n = \Sigma M_x N_x / \Sigma N_x \qquad (9)$$
$$M_w = \Sigma M_x^2 N_x / \Sigma M_x N_x \qquad (10)$$
$$M_z = \Sigma M_x^3 N_x / \Sigma M_x^2 N_x \qquad (11)$$

where M_x is the molecular weight of an x-mer molecule and N_x is the number of x-mers. The "number-average" molecular weight, M_n, may be obtained by ordinary physical or chemical methods (end group determination, osmotic pressure measurement, etc.); the "weight-average" molecular weight, M_w, and the "Z-average" molecular weight, M_z, can be evaluated from sedimentation equilibrium measurements in the ultracentrifuge. M_w may also be determined by means of Staudinger's[17] viscosity method (cf. seq.) in cases where this method is capable of yielding valid results.

These molecular weight averages may be evaluated in terms of p by substituting equation (3) for N_x, and $x M_0$ for M_x, the molecular weight of an x-mer molecule, where M_0 is the molecular weight of one segment.[18] These substitutions lead to the equations

$$M_n = M_0 \Sigma x p^{x-1}(1-p)^2 / \Sigma p^{x-1}(1-p)^2$$
$$M_w = M_0 \Sigma x^2 p^{x-1}(1-p)^2 / \Sigma x p^{x-1}(1-p)^2$$
$$M_z = M_0 \Sigma x^3 p^{x-1}(1-p)^2 / \Sigma x^2 p^{x-1}(1-p)^2$$

It can be shown that the values of the summations are as follows

$$\Sigma p^{x-1}(1-p)^2 = 1 - p$$
$$\Sigma x p^{x-1}(1-p)^2 = 1$$
$$\Sigma x^2 p^{x-1}(1-p)^2 = (1+p)/(1-p)$$
$$\Sigma x^3 p^{x-1}(1-p)^2 = (1+4p+p^2)/(1-p)^2$$

Substituting these values in the equations for M_n, M_w and M_z

$$M_n = M_0/(1-p) \qquad (12)$$
$$M_w = M_0(1+p)/(1-p) \qquad (13)$$
$$M_z = M_0(1+4p+p^2)/(1-p^2) \qquad (14)$$

Also

$$M_n : M_w : M_z = 1 : (1+p) : (1+4p+p^2)/(1+p) \qquad (15)$$

The divergence among the three average molecular weights is a measure of the non-homogeneity of the polymer, and from it Lansing and Kraemer[3c] derive their "non-uniformity coefficient." The three averages are all equal when $p = 0$. As the polymerization proceeds and p increases, M_w becomes progressively greater than M_n, and M_z becomes greater than M_w. When p is close to unity, i. e., when the average molecular weight is high, the ratio (15) becomes approximately

$$M_n : M_w : M_z = 1 : 2 : 3 \qquad (15b)$$

It will be well to emphasize the bearing of these results on Staudinger's method for determining molecular weights of linear polymers from the viscosities of their dilute solutions. He has advocated the use of the following relation for the determination of the average molecular weight of linear polymeric substances

$$K M_n = \left(\frac{\eta_r - 1}{c}\right)_{(c \to 0)}$$

where η_r is the relative viscosity, c is the concentration, and K is the Staudinger constant. Without taking into account different averages, Staudinger has used the common number-average molecular weight in the above equation. Kraemer and Lansing[19] have shown that the weight-average molecular weight, M_w, should be used in this equation instead of M_n. Therefore, only in cases where the ratio M_w/M_n is constant can it also be presumed that $[(1-\eta_r)/c]_{(c=0)}$ will be proportional to M_n. As shown above, this ratio does become very nearly constant (equal to two) for high molecular weight polymers of the type considered here. Hence, though the Staudinger equation may be applicable to high molecular weight polymers of this type, when the molecular weight is low (when $p < 0.9$ and $M_n/M_0 < 10$), the use of this equation is no longer permissible. In its stead, one should use the equation

$$\left(\frac{\eta_r - 1}{c}\right)_{(c \to 0)} = K' M_w = K'(1+p)M_n$$

where $K' = \frac{1}{2}K$. It would be interesting to trace experimentally the deviation from the

(17) Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932.

(18) M_x may not equal $x M_0$ exactly inasmuch as the molecular weight of terminal groups (H and —OH in the case of polyesters) is neglected. However, for large molecules the discrepancy will be very small. If two kinds of segments are present (case (ii)), then M_0 must be taken as the mean molecular weight of the segments.

(19) Kraemer and Lansing, J. Phys. Chem., 39, 153 (1935); see also Kern, Ber., 68, 1439 (1935), and the work of Schulz on vinyl polymers.

Staudinger equation in the range of low molecular weights.

Type (ii) Polymers Prepared from Non-equivalent Amounts of the Reactants.—As was described in the introduction, three kinds of molecules may be formed in type (ii) polymerizations: molecules composed of an even number of segments ("*even*" x-mers), molecules composed of an odd number of segments and terminated by A groups ("*odd*-A" x-mers), and molecules containing an odd number of segments and terminated by B groups ("*odd*-B" x-mers). When an excess of one reactant, arbitrarily chosen here as the reactant designated by B—B, is used, separate functions must be derived for each of the three kinds of molecules. The following modified terminology will be used.

N_0' = number of A groups = twice number of A—A segments.

N_0'' = number of B groups = twice number of B—B segments.

N' and N'' are the numbers of the respective unreacted functional groups.
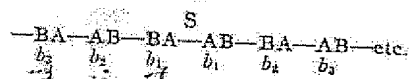
$N_0'' - N_0' = N'' - N' = n$ = excess of B—B segments.

p = probability that an A group has reacted = $(N_0' - N')/N_0'$

q = probability that a B group has reacted

$= \dfrac{N_0'' - N''}{N_0''} = \dfrac{N_0' - N'}{N_0''} = rp$

where $r = N_0'/N_0''$.

In analogy to the method of derivation used formerly, a single segment S is selected at random from the sequence of segments

$$\overset{}{-}\text{BA}-\text{AB}-\text{BA}-\overset{\text{S}}{\text{AB}}-\text{BA}-\text{AB}-\text{etc.}$$
$$\underset{b_{-3}}{}\ \underset{b_{-2}}{}\ \underset{b_{-1}}{}\ \underset{b_1}{}\ \underset{b_2}{}\ \underset{b_3}{}$$

and the probability that it is a component of an x-mer is determined by adding the probabilities of each configuration which will meet this requirement. Because of the different varieties of polymers (see (iia) and (iib)) and the non-interchangeability of A—A and B—B when the latter are in excess, it will be necessary to use superscripts and subscripts to designate the various Π_x's, N_x's and P_x's which arise.

First, molecules for which x is an even integer will be considered. If the segment S selected at random happens to be an A—A, the probability that there is linkage at b_1 is p, at b_2 it is q, at b_3 it is p, etc., alternately. A similar rule applies to b_{-n}, and so we have p for the probability of linkage where n is odd (either + or −) and q where n is even. For each of the x configurations which will include S in the *even* x-mer, there will be $x/2$

links where n is odd, $(x/2) - 1$ links where n is even, and one of the terminal groups will be A and the other B. The probability that any given A—A segment is a component of an *even* x-mer is, therefore

$$\Pi_x'(even) = xp^{x/2}q^{(x/2)-1}(1-p)(1-q)$$
$$= xp^{x-1}r^{(x/2)-1}(1-p)(1-rp) \quad (16)$$

If a B—B group had been selected as the segment S, the same considerations would apply with p and q interchanged. That is, if A's and B's were interchanged in the chain of segments pictured above then S would become a B—B segment, q would be the probability of linkage at b_n when n is odd, and p would be the probability when n is even. By interchanging p and q in (16) the probability, $\Pi_x''(even)$, that any given B—B segment is a part of an *even* x-mer is obtained.

$$\Pi_x''(even) = xp^{x-1}r^{x/2}(1-p)(1-rp) = r\Pi_x'(even) \quad (17)$$

The total number of segments in *even* x-mers =

$$xN_x(even) =$$
$$(N_0'/2)\Pi_x'(even) + (N_0''/2)\,\Pi_x''(even)$$

Substituting (16) and (17) and recalling that $rN_0'' = N_0'$

$$N_x(even) = \frac{N_0'\Pi_x'(even)}{x} =$$
$$N_0'p^{x-1}r^{x/2}[(1-p)(1-rp)r^{-1}] \quad (18)$$

For the fraction of the total number of *both* kinds of segments which are contained in *even* x-mers

$$\Pi_x(even) = \frac{xN_x(even)}{1/2\,(N_0' + N_0'')}$$

Substituting $N_0' + N_0'' = N_0'(1+r)/r$ in the above

$$\Pi_x(even) = xp^{x-1}r^{x/2}\frac{2(1-p)(1-rp)}{1+r} \quad (19)$$

$\Pi_x(even)$ is the approximate weight fraction of an *even* x-mer (21).

For the mole fraction of *even* x-mer

$$P_x(even) = \frac{N_x}{\text{Total no. of molecules}} = \frac{N_x}{1/2(N' + N'')}$$
$$N' = (1-p)N_0'$$
$$N'' = (1/r - p)N_0'$$

From (18), therefore

$$P_x(even) = p^{x-1}r^{x/2}\left[\frac{2(1-p)(1-rp)}{(1+1/r-2p)r}\right] \quad (20)$$

When x is odd the number of links is even and the two terminal groups are either both A's or both B's (see (iib)). First, let us find the probability, $\Pi_x'(odd\text{-}A)$, that an A—A segment such as S is a component of an *odd* x-mer having A groups at its ends. Each of the $(x + 1)/2$ configurations fulfilling this requirement contains

$(x - 1)/2$ links at b_n's where n is odd and $(x - 1)/2$ links where n is even. Therefore

$$\Pi_x'(odd\text{-}A) = \left(\frac{x+1}{2}\right)(pq)^{(x-1)/2}(1 - p)^2$$
$$= \left(\frac{x+1}{2}\right)p^{x-1}r^{(x-1)/2}(1 - p)^2 \qquad (21)$$

There are $(x - 1)/2$ configurations containing the A—A segment, S, which give odd x-mers having B end groups. For each of these there are $(x + 1)/2$ links where n is odd and $(x - 3)/2$ where n is even. Consequently

$$\Pi_x'(odd\text{-}B) = \frac{x-1}{2}\,p^{x-1}\,r^{(x-3)/2}(1 - rp)^2 \qquad (22)$$

To find the corresponding probabilities that a B—B segment is a component of an odd x-mer, A is interchanged with B and p with q, as was done above. When A and B are interchanged in configurations giving odd-A terminated x-mers, odd-B terminated x-mers result. By interchanging p and q in (21) one gets the probability, $\Pi_x''(odd\text{-}B)$, that any given B—B segment is contained in an odd x-mer terminated with B groups.

$$\Pi_x''(odd\text{-}B) = \frac{x+1}{2}\,p^{x-1}\,r^{(x-1)/2}(1 - rp)^2 \qquad (23)$$

Similarly by interchanging p and q in $\Pi_x'(odd\text{-}B)$ one gets

$$\Pi_x''(odd\text{-}A) = \frac{(x-1)}{2}\,p^{x-1}\,r^{(x+1)/2}(1 - p)^2 \qquad (24)$$

The total number of segments contained in odd x-mers terminated with A groups is given by $xN_x(odd\text{-}A) = \frac{1}{2}N_0'\,\Pi_x'(odd\text{-}A) + \frac{1}{2}N_0''\,\Pi_x''(odd\text{-}A)$. Replacing N_0'' by N_0'/r and introducing (21) and (24)

$$N_x(odd\text{-}A) = N_0'\,p^{x-1}\,r^{x/2}\,[1/2(1 - p)^2\,r^{-1/2}] \qquad (25)$$

Similarly

$$N_x(odd\text{-}B) = N_0'\,p^{x-1}\,r^{x/2}\,[1/2(1 - rp)^2\,r^{-1/2}] \qquad (26)$$

The corresponding Π_x's are

$$\Pi_x(odd\text{-}A) = \frac{xN_x(odd\text{-}A)}{1/2(N_0' + N_0'')}$$
$$= xp^{x-1}r^{x/2}\left[\frac{(1 - p)^2\,r^{1/2}}{1 + r}\right] \qquad (27)$$

and

$$\Pi_x(odd\text{-}B) = xp^{x-1}r^{x/2}\left[\frac{(1 - rp)^2}{1 + r}\,r^{-1/2}\right] \qquad (28)$$

The mole fractions $P_x(odd\text{-}A)$ and $P_x(odd\text{-}B)$ can be derived from (25) and (26) in the same way that (20) was obtained from (18).

$$P_x(odd\text{-}A) = p^{x-1}\,r^{x/2}\left[\frac{(1 - p)^2\,r^{-1/2}}{1 + 1/r - 2p}\right] \qquad (29)$$

and

$$P_x(odd\text{-}B) = p^{x-1}\,r^{x/2}\left[\frac{(1 - rp)^2\,r^{-3/2}}{1 + 1/r - 2p}\right] \qquad (30)$$

Overlooking for the moment that x cannot assume the same integers in both even and odd functions, (19), (27) and (28) lead to the ratio

$$\Pi_x(even):\Pi_x(odd\text{-}A):\Pi_x(odd\text{-}B) =$$
$$2(1 - p)(1 - rp):(1 - p)^2 r^{1/2}:(1 - rp)^2\,r^{-1/2} \quad (31)$$

which is independent of x. The corresponding ratios for the N_x's and P_x's are identical with the above ratio.

Substituting $p = 1$ in the above equations to obtain distributions at completion of the reaction

$$\Pi_x(even) = \Pi_x(odd\text{-}A) = 0$$
$$P_x(even) = P_x(odd\text{-}A) = 0$$
$$\Pi_x(odd\text{-}B) = xr^{x/2}(1 - r)r^{-1/2}/(1 + r) \qquad (28b)$$
$$P_x(odd\text{-}B) = r^{x/2}(1 - r)r^{-1/2} \qquad (30b)$$

The complete absence of even and odd-A molecules is a consequence of the reaction of all A groups.

To summarize the above equations, (18), (19) and (20) give, respectively, the numbers, the weight fractions and the mole fractions of even molecules. The corresponding quantities for odd-A molecules are given by (25), (27) and (29), and for odd-B molecules by (26), (28) and (30). The distributions at completion of the reaction ($p = 1$) are given by (28b) and (30b).

The weight fraction distribution functions are plotted in Fig. 6 for $r = 0.80$ (25% excess of B—B molecules) at the three stages of the reaction, $p = 0.85$, 0.95 and 1.00. All three curves for a given pair of r and p values are similar in the sense that, as shown by (30), for all x values the ratio of the three Π_x's is the same. Consequently, all three maxima come at the same molecular size (x value). In Fig. 7 the weight-fraction of x-mer (odd-B only, since all other types are absent) is plotted against x at complete reaction (equation (28b)) for several values of r. The method of area summation given above can be applied in these figures also.

For any value of r there are present initially ($p = 0$) only odd-A (A—A) and odd-B (B—B) molecules, and even molecules are absent entirely. If the numbers of the two kinds of segments are equal ($r = 1$), the amount of even polymer will increase steadily (starting from zero) as the reaction progresses, until the amounts of even and odd (odd-A plus odd-B) molecules become practically equal. With an excess of B—B segments present, the amount of even polymer increases until a maximum is reached and then decreases steadily, returning to zero when $p = 1$. At this maximum the amount of even polymer may or may not be greater than the amount of odd-B polymer, but

for all values of p the amount of *even* polymer is less than the amount of BOTH kinds of *odd* polymer. The amount of *odd*-A polymer is always less than the amount of *odd*-B polymer and the ratio of the former to the latter becomes less as p

Fig. 6.—Weight fraction distribution curves for a 25% excess of B groups ($r = 0.80$). When $p = 0.85$ - - - -, $p = 0.95$ ———— and $p = 1.00$ ————. Curves labeled "even" are for *even* molecules, *i. e.*, those having an even number of segments; those labeled "odd-A" are for *odd* molecules having A groups as termini, and those labeled "odd-B" are for *odd*, B terminated molecules. The even curves apply for even integers only, the odd curves for odd integers only. One square = 0.005 weight fraction.

increases. These characteristics are illustrated in Fig. 6.

When equivalents of the reactants are used, the number-average molecular weight is

$$M_n = \frac{M_0(N_0' + N_0'')}{N' + N''} = M_0(1+r)/(1+r-2rp) \quad (32)$$

where M_0[20] is the average molecular weight of one segment. When $r = 1$ this equation reduces to (12). At completion of the reaction when $p = 1$

$$M_n = M_0(1+r)/(1-r) \quad (32b)$$

This equation shows the effect of an excess of one reactant in limiting the maximum molecular weight which can be reached.

The type of distribution of molecules obtained when an excess of one reactant is used closely simulates the distribution in polymers formed

(20) In this case, $M_0 = \dfrac{M_0'N_0' + M_0''N_0''}{N_0' + N_0''}$ where M_0' and M_0'' are the respective molecular weights of the two segments as contained within a polymer molecule.

from exact equivalents. (Compare curves in Figs. 6 and 7 with those in Figs. 1 and 2.) The dependence of weight fraction, or mole fraction, on x is of the same type; the principal difference lies in the replacement of p by $r^{1/2}p$. It can be shown that if $r^{1/2}p$ for one polymer equals $r^{1/2}p$ for another polymer, then their average molecular weights will be nearly the same (except when $r^{1/2}p$ is much less than unity), the maxima in their Π_x *vs.* x curves will occur at the same x value, and the distribution curves will vary with x in a similar way. The two distributions will differ only in the ratio of the quantities of the three kinds of molecules, *even*, *odd*-A and *odd*-B (2:1:1 for $r = 1$). Thus, for example, for a particular *even* value of x there will be fewer *even* x-mers contained in a polymer for which $r = r_1$ than in another polymer of the same average molecular weight (*i. e.*, the same $r^{1/2}p$ value) but for which $r = r_2 > r_1$; but the amount of *odd* $(x + 1)$-mers in the former polymer will be greater by a corresponding amount (unless M_n is very low). Unless the method of examination of the two polymers is sufficiently precise to differentiate consecutive members in the sequence of sizes, the two distributions will appear to be identical if $r^{1/2}p$ of one equals $r^{1/2}p$ for the other.
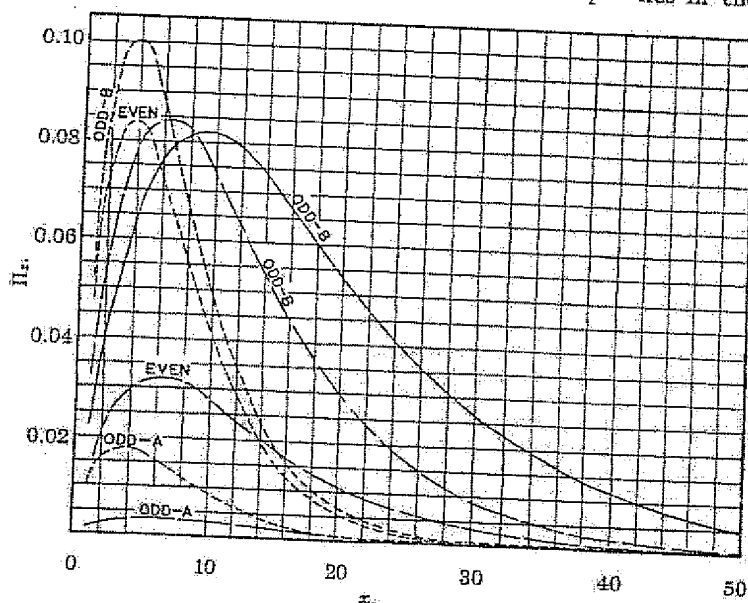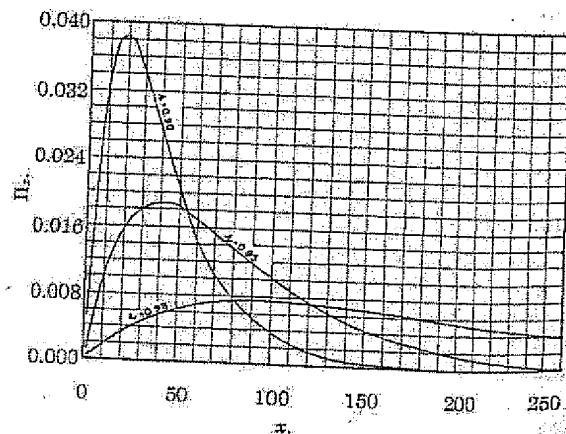

Fig. 7.—Weight fractions at completion of the reaction ($p = 1$) for several values of r. Only odd integral values of x are significant. One square = 0.01 weight fraction.

The distribution functions possess maxima characteristics similar to those previously discussed for "$r = 1$" polymers. In fact, the same equations may be used for locating the x_{max} value for Π_z by replacing p with $r^{1/2}p$. Exact equations for M_w and M_z, corresponding to equations (13) and (14), are cumbersome; for all practical purposes it is permissible merely to replace p with $r^{1/2}p$ in (13) and (14), respectively. It follows that here also the ratio of $M_n : M_w : M_z$ approaches $1:2:3$ for high molecular weights. Thus, sedimentation equilibrium measurements in the ultracentrifuge would not distinguish the two types of polymers.

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Summary

1. Equations expressing the weight fraction, number, and mole fraction of each molecular species in a linear condensation polymer have been derived on the basis of simple and not improbable assumptions. The characteristics of these functions have been demonstrated and discussed.

2. The number-average, weight-average and Z-average molecular weights of Lansing and Kraemer are shown to be in the ratio $1:2:3$ for the high molecular weight polymers. The bearing of this result on Staudinger's method for determining molecular weights has been discussed.

3. The special case of polymers prepared by the condensation of non-equivalents of two bifunctional reactants (A—A + B—B) has been analyzed and shown to conform to a distribution similar to the above. Other special cases can be subjected to a similar analysis.
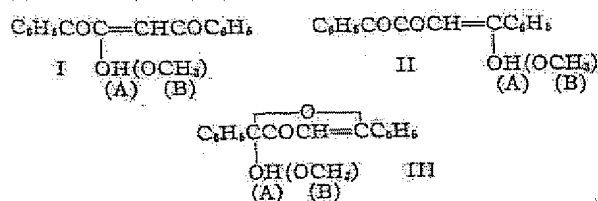
WILMINGTON, DEL.   RECEIVED MARCH 24, 1936

Further Studies on 1,4-Diphenyl-1,2,4-butanetrione Enol, Including Alkylation and Benzoylation

BY ROBERT E. LUTZ AND ALFRED H. STUART

Two methyl ethers have been obtained from the enol. One of these, dibenzoylmethoxyethylene I(B), the structure of which is certain, was made directly by the action of diazomethane.[1b] The other, a structural isomer II(B) or III(B), was obtained by the action of methanol and acid on the enol or various of its derivatives and was believed to have the open chain structure II(B) because it gave methyl benzoate on ozonization;[1b] however, the alternative cyclic structure III(B),[2] which was not considered at that time, also would account for this result.

The ease of formation of the isomeric ether by catalytic etherification does not distinguish between the two formulations II(B) and III(B) since there is analogy for the reaction in both open chain and cyclic types (cf. hydroxynaphthoquinone[3] and the sugars). The quinoxaline reaction, however, which is specific for α-diketones, has been used.[2b]

o-Phenylenediamine reacts readily with the enol to give a quinoxaline (IV) which is bright orange in color in contrast with other quinoxalines of this series. Oxidation of this product by means of chromic acid gives the carboxy and

$C_6H_5COC=CHCOC_6H_5$
I $OH(OCH_3)$
(A) (B)

$C_6H_5COCOCH=CC_6H_5$
II $OH(OCH_3)$
(A) (B)

$C_6H_5CCOCH=CC_6H_5$ (with O bridge)
III $OH(OCH_3)$
(A) (B)
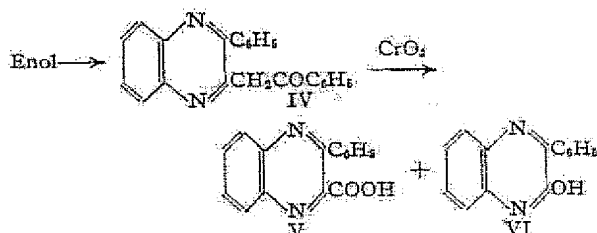

(1) Cf. (a) Lutz, THIS JOURNAL, 56, 1590 (1934); (b) Lutz, Wilder and Parrish, ibid., 56, 1980 (1934); Lutz and Wilder, ibid., 56, (c) 1987, (d) 2065, (e) 2145 (1934).
(2) Cf. (a) Blatt, ibid., 57, 1103 (1935); (b) Köhler, Westheimer and Tishler, ibid., 58, 264 (1936).
(3) Fieser, ibid., 48, 2922, 3201 (1926).